Statistical Thermodynamics in Chemistry and Biology

25. Phase transitions

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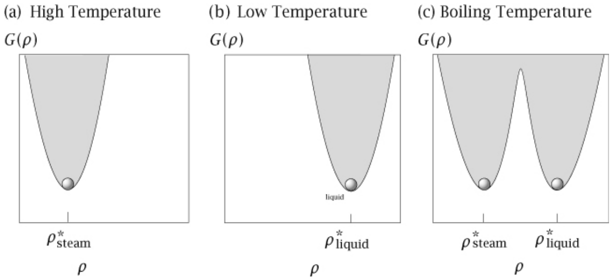
Phase transitions

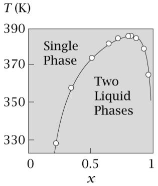
This chapter:

- Introduction to phase transitions
- Two states can be stable at the same time
- As usual, the free energy is minimized
- The free energy curve may have several minima



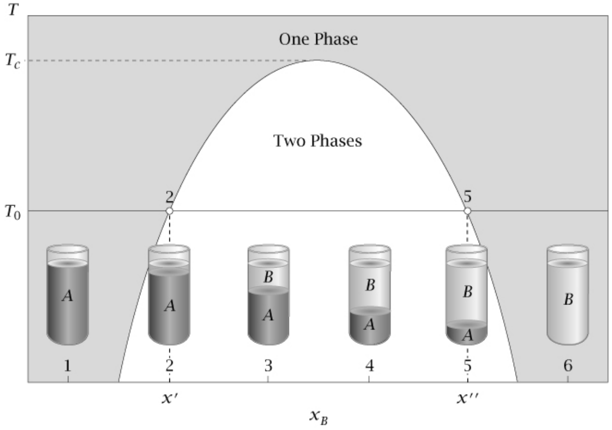
Temperature dependence

- Oil and water form two phases in equilibrium.
- A phase diagram is shown in the figure.
- The temperature dependence is demonstrated.



Experiment to create phase diagram

- Six bottles with different oil fraction, x, a temperature, T_0.



Experiment to create phase diagram

Part 2

- Exp. 1. Small fraction of oil. Everything dissolved in water.
- Exp. 2. Happens to be exactly where a second phase appears. It marks the phase boundary. The fraction of oil in the water-rich phase is x'.
- Exp. 3. Two phase solution. The fraction of oil in the water-rich phase is x'. The fraction of oil in the oil-rich phase is x''.
- Exp. 4. Two phase solution. The fraction of oil in the water-rich phase is x'. The fraction of oil in the oil-rich phase is x''. The amount of the various phases have shifted.
- Exp. 5. Happens to be exactly where the second phase vanishes. It marks the phase boundary. The fraction of oil in the oil-rich phase is x''.
- Exp. 6. Large fraction of oil. All water dissolved in oil.

Experiment to create phase diagram

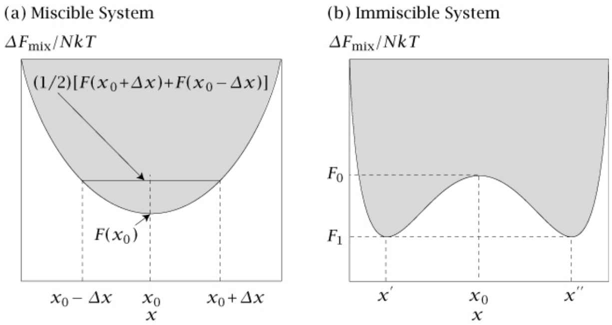
Part 3

- The phase boundary is also called the solubility curve or coexistence curve.
- In the coexistence region we have two phases in equilibrium.
- We have a critical temperature, T_C. Above T_C the two components are miscible at all proportions.

Lattice model for phase separation

- The free energy of mixing for a lattice model (Eq. 15.16),

$$\frac{\Delta F_{\text{mix}}}{N} = k_B T x \ln x + k_B T (1-x) \ln (1-x) + k_B T \chi_{AB} x (1-x)$$



Lattice model for phase separation

Part 2

- Note that the energy term is not temperature dependent (in the mean-field model) since

$$\chi_{AB} = \frac{z}{k_B T}\left(w_{AB} - \frac{w_{AA} + w_{BB}}{2}\right)$$

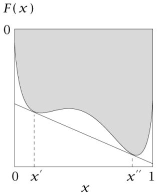
- The way to think about it: (left figure, previous slide)

$$\frac{1}{2}F(x_0 + \Delta x) + \frac{1}{2}F(x_0 - \Delta x) > F(x_0)$$

  i.e. two phases with compositions $x_0 + \Delta x$ and $x_0 - \Delta x$ have a higher free energy than one phase with composition x_0.
- On the other, for the figure to the right, it is possible to find a composition of two phases, $F(x')$ and $F(x'')$, with lower free energy than $F(x_0)$.
- Also note that we have a criteria for stability,

$$\left(\frac{\partial^2 F}{\partial x^2}\right)_{x_0} > 0$$

Predict the compositions



- The compositions x' and x'' can be found by drawing the tangent to $F(x)$ at two points.
- Why? Regard the free energy

$$F = N(\mu_A x_A + \mu_B x_B) = N x_B(\mu_B - \mu_A) + N\mu_A$$

- We also have

$$\frac{\partial F}{\partial x_B} = N(\mu_B - \mu_A)$$

- At a two-phase equilibrium, the chemical potential of each component must be the same in both phases,

$$\mu_A' = \mu_A'' \, , \; \mu_B' = \mu_B'' \quad \Rightarrow \quad \mu_B' - \mu_A' = \mu_B'' - \mu_A''$$

- This leads to $\left(\frac{\partial F}{\partial x_B}\right)_{x'} = \left(\frac{\partial F}{\partial x_B}\right)_{x''}$, which is close to, but not necessarily the same as, the local minimum points.

The lever rule: the amount of the two stable phases

- Take Exp. 3 as an example
- We would like to get the fraction, f,

$$f = \frac{\text{number of molecules in A-rich phase}}{\text{total number of molecules in both phases}}$$

- We also have

$$x' = \frac{\text{number of B molecules in A-rich phase}}{\text{number of molecules in A-rich phase}}$$

- so

$$fx' = \frac{\text{number of B molecules in A-rich phase}}{\text{total number of molecules in both phases}}$$

- Using the same procedure,

$$(1-f)x'' = \frac{\text{number of B molecules in B-rich phase}}{\text{total number of molecules in both phases}}$$

- Combining the last two expressions,

$$fx' + (1-f)x'' = x_0 = \frac{\text{number of B molecules in both phases}}{\text{total number of molecules in both phases}}$$

The lever rule: the amount of stable phase

Part 2

- This leads to the lever rule

$$f = \frac{x_0 - x''}{x' - x''}$$

To summarize: we know how to obtain

- the compositions of each phase, x' and x''
- the amount of each phase

Summary

- Brief introduction to phase transitions and phase diagrams
  - Predict compositions of each phase
  - Lever rule: the amount of each phase

Not included ... but perhaps you will hear about it in the future

- Spinodal curves
- More about critical points and critical temperatures

Exam June 2014: Exercise 3

We will try to mix two liquids A and B. In terms of the Helmholtz free energy, what is the distinction between a mixture and a two-phase system? For a two-phase system, briefly explain (not derive) how the composition of the two phases and the relative amount of each phase can be obtained, respectively. What is the definition of the critical temperature for a two-phase system?